INTRODUCTION TO CHEMICAL EQUILIBRIA AND ACTIVITY MODELLING

Activity modelling is used to determine equilibrium lines between pairs of minerals in a chemical system, *e.g.*, the reaction between talc (Tlc) and magnesite (Mgs):

$$Mg_3Si_4O_{10}(OH)_{2(s)} \text{ (Tlc)} + 3\ CO_{2(g)} + 7\ H_2O = 3\ MgCO_{3(s)} \text{ (Mgs)} + 4H_4SiO_{4(aq)}$$

[1]
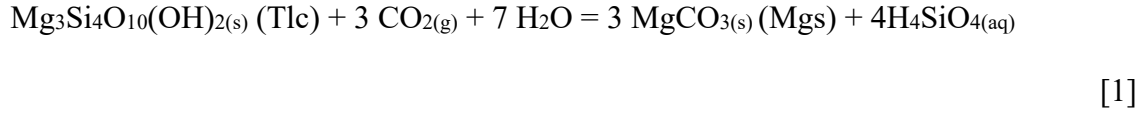
The equilibrium constant of this reaction at a given pressure and temperature ($K_{P,T}$) is expressed as the activity of the products divided by the activities of the reactants:

$$K_{P,T} = \frac{a_{MgCO_3}^3\, a_{H_4SiO_4(aq)}^4}{a_{Mg_3Si_4O_{10}(OH)_2}\, f_{CO_2}^3\, a_{H_2O}^7};$$

[2]

where a_X represents the activity of a given phase X, and the exponent represents the stoichiometric coefficient of the phase. Taking the logarithm of both sides yields:

$$\log K_{T,P} = 3\log a_{MgCO_3(s)} + 4\log a_{H_4SiO_4(aq)} - \log a_{Mg_3Si_4O_{10}(OH)_2(s)} - 3\log f_{CO_2(g)}$$

$$- 7\log a_{H_2O(l)}.$$

[3]

Of particular interest is the effect of CO_2 fugacity and $H_4SiO_{4(aq)}$ activity on the stability of talc *versus* magnesite. Therefore, [3] can be rewritten in the form of $y = mx + b$ with $\log f_{CO_2(g)}$ as the independent variable x and $\log a_{H_4SiO_4(aq)}$ as the dependent variable y:

$$\log a_{H_4SiO_4(aq)} = \frac{3}{4}\log f_{CO_2(g)}$$

$$+ \frac{1}{4}\left[\log K_{T,P} - 3\log a_{MgCO_3(s)} + \log a_{Mg_3Si_4O_{10}(OH)_2(s)} + 7\log a_{H_2O(l)}\right].$$

[4]

Supplementary File 1: Introduction to chemical equilibria and activity modelling

Assuming the activities for pure solids and liquids is unity, *i.e.*, $\log a_{H_2O(l)} = \log a_{MgCO_3(s)} = \log a_{Mg_3Si_4O_{10}(OH)_2(s)} = 0$ (assuming no solid solution) leads to a simplified expression:

$$\log a_{H_4SiO_4(aq)} = \frac{3}{4}\log f_{CO_2(g)} + \frac{1}{4}\left[\log K_{T,P}\right].$$

[5]

Graphically, this represents a line with a slope of $\frac{3}{4}$ and intercept of $\frac{1}{4}\left[\log K_{T,P}\right]$. Plotting these lines for each set of phases produces an activity diagram.

To plot this line, the value of $\log K_{T,P}$ must be determined. At equilibrium, $\log K_{T,P}$ is directly proportional to the standard molar Gibbs free energy of the reaction ($\Delta_r G_{P,T}^0$):

$$\Delta_r G_{P,T}^0 = -\ln(10)\,RT\log K_{T,P}\,;$$

[6]

where R is the ideal gas constant (8.314 J·K⁻¹·mol⁻¹). The $\Delta_r G_{T,P}$ can be determined by stoichiometric sum of the apparent molar Gibbs free energy of formation ($\Delta_a G_{T,P}$) values for the products minus those of the reactants.

The $\Delta_a G_{P,T}$ of each mineral and phase at the P, T of interest is given by the Legendre transform of the fundamental equation of thermodynamics (first and second laws of thermodynamics; *e.g.*, Berman 1988):

$$\Delta_a G_{P,T}^0 = \Delta_f H_{P,T}^0 - TS_{P,T}^0;$$

[7]

where $\Delta_f H_{P,T}^0$ = enthalpy of formation at the P and T of interest; and $S_{P,T}^0$ = entropy at the P and T of interest.

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The values for $\Delta_f H_{T,P}$ and $S_{T,P}$ are related to the standard state enthalpy of formation measured at reference conditions of 1 bar and 25°C ($\Delta_f H_{P_r,T_r}^0$ and S_{P_r,T_r}^0, resp.), by considering the changes in H and S as a function of P and T (e.g., Berman 1988):

$$\Delta_a G_{P,T}^0 = \Delta_f H_{P_r,T_r}^0 - T S_{P_r,T_r}^0 + \int_{T_r}^{T} C_P \, dT - T \int_{T_r}^{T} \frac{C_P}{T} \, dT + \int_{P_r}^{P} V \, dP;$$

[8]

where: P_r, T_r = reference pressure (1 bar) and temperature (25°C); P, T = pressure and temperature of interest; C_P = heat capacity at constant pressure (i.e., isobaric); and V = volume. Note that the superscripted zero refers only to pure standard-state quantities and does not refer to the standard P-T conditions as usually denoted in physical chemistry. Given the above thermodynamic data, it is possible to calculate $\Delta_a G_{P,T}^0$ for each phase component in the reaction, yielding $\Delta_r G_{P,T}^0$ and $\log K_{T,P}$, which permits the plotting of the equilibrium line for talc versus magnesite in the above example.

From [8], the $\int_{T_r}^{T} C_P \, dT - T \int_{T_r}^{T} \frac{C_P}{T} \, dT$ terms require an equation of state for C_P vs. T. The value of C_P is variably expressed as polynomial functions of T of the form:

$$C_P = a + bT + cT^{-2} + dT^{-0.5} + eT^2 + fT^{-3} + gT^{-1};$$

[9]

where a, b, c, d, e, f, and g are phase-specific empirical coefficients. Commonly used conventions include: (1) Maier-Kelley ($C_P = a + bT + cT^{-2}$, Maier & Kelley 1932), (2) Haas-Fisher ($C_P = a + bT + cT^{-2} + dT^{-0.5} + eT^2$, Haas & Fisher 1976, Robie & Hemingway 1995), (3) Berman-Brown ($C_P = a + dT^{-0.5} + cT^{-2} + fT^{-3}$, Berman & Brown 1985), and (4) Holland-Powell ($C_P = a + bT + cT^{-2} + dT^{-0.5}$; Holland & Powell 1985, Powell & Holland 1985). Where heat

capacity data are not available, some thermodynamic data use the constant isobaric heat capacity assumption ($C_P = a$) or the Van't Hoff approximation ($C_P = 0$).

Similarly, the $\int_{P_r}^{P} V \, dP$ term in [8] requires an equation of state for the relationship between V vs. P and T. Many thermodynamic databases assume constant V for solids, given the minor deviations from surface conditions (e.g., up to 5 kbar and 1000 °C). However, it is invalid to extrapolate constant V from surface conditions to the greater metamorphic P-T conditions (e.g., to 100 kbar and 1000 °C), so equations of state for V have been implemented in metamorphic databases. For example, Berman (1988) uses the following relation:

$$\frac{V^{P,T}}{V^{P_r,T_r}} = 1 + v_1(P - P_r) + v_2(P - P_r)^2 + v_3(T - T_r) + v_4(T - T_r)^2,$$

[10]

where v_1, v_2, v_3, and v_4 are empirical coefficients which describe the isothermal (v_1, v_2) and isobaric (v_3, v_4) compressibilities of the mineral of interest. Holland and Powell (1990, 1998, 2011) use more complex equations of state for V, but discussion of these is beyond the scope of this contribution.

For aqueous species, the refined Helgeson-Kirkham-Flowers (HKF) equations of state may be used instead of the heat capacity and volume equations of state listed above (Helgeson et al. 1981, Tanger & Helgeson 1988). The equations of state are built on the Born equation, which involves the Born solvation coefficient ω; non-solvation volume coefficients a_1, a_2, a_3, a_4; and non-solvation heat capacity coefficients c_1, c_2; and charge Z (see Sverjensky 2019 for a comprehensive overview; Helgeson & Kirkham 1976).

As a note, caution must be taken when entering C_P and HKF coefficients from a thermodynamic database into a thermodynamic modelling software package because some of the

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C_P and HKF coefficients are reported in differing orders of magnitude (*e.g.*, for Maier-Kelley coefficients, b is commonly multiplied by 10^{-3} and c by 10^{-5}). Equally, it is important to check that the coefficient matches the correct corresponding polynomial in the equation for the C_P coefficients being selected.

Thus, for all chemical species, the following data are needed: $\Delta_f H^0_{Pr,Tr}$, $S^0_{Pr,Tr}$, C_P, and V ($\Delta_a G^0_{Pr,Tr}$ can be calculated from the above data). Note that the S value used in aqueous geochemistry (Benson 1968, Helgeson *et al.* 1978) follows a different convention than that for metamorphic petrology (Powell & Holland 1985, Berman 1988). In metamorphic petrology, S is calculated using the third law of thermodynamics ($S^0_{Pr,Tr} = \int_0^{Tr} \frac{C_P}{T} dT$) and does not include the entropies of the elements (S_{el}), whereas aqueous geochemistry includes the stoichiometric sum ($\sum_{el} n_{el}$) of S_{el} ($\Delta_f S^0_{Pr,Tr} = \int_0^{Tr} \frac{C_P}{T} dT - \sum_{el} n_{el} S_{el}$), so it is necessary to verify that the database and software are using the same convention. For minerals and gases, both the coefficients expressing C_P as a function T, and the equation of state for V as a function of P and T are needed (if no relation for V is given, it is assumed to be constant). For aqueous species, the HKF coefficients (a_1, a_2, a_3, a_4, c_1, c_2, ω, and Z) may be used. Note that some software packages and thermodynamic databases do not use this thermodynamic data *per se*, instead employing the $\log K$ values related to the formation of minerals at various temperatures (*e.g.*, The Geochemist's Workbench™; Bethke 1995). Additionally, some $\log K$ databases account for the effects of P on $\log K$ to < 1 kbar (*e.g.*, *PHREEQC*); Appelo *et al.* 2014).

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